

PATENT ABSTRACTS OF JAPAN

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(54) CHROMIUM PLATING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a flawless chromium plating film excellent in corrosion resistance in the chromium plating method by dispersing a superfine grain insoluble in a plating soln. in a sergeant bath consisting essentially of chromic anhydride or further forming a current into a pulse shape in plating.

SOLUTION: A sergeant bath consisting essentially of chromic anhydride is used in the chromium plating method, and plating is conducted while impressing a pulsating current of 100Hz to 3kHz. Otherwise, the superfine grain of Al₂O₃ or SiO₂ insoluble in a plating soln. and having 1μm diameter is dispersed in the sergeant bath, and chromium plating is performed while impressing a pulsating current of 100Hz to 3kHz.

Reference 6

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(54) 【発明の名称】 クロムめっき方法

(57) 【要約】

【課題】 無欠陥で耐食性に優れたクロムめっき皮膜を形成する方法に関する。

【解決手段】 ①無水クロム酸を主成分とするサージェント浴を使用し、パルス電流を印加しつつめっき処理するか、②同サージェント浴に該浴に不溶解性の超微粒子を分散させてめっき処理して目的クロムめっきを得る方法。

JAPANESE [JP,09-170095,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS OPERATION EXAMPLE DESCRIPTION OF
DRAWINGS DRAWINGS

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1]A chromium plating method characterized by carrying out plating processing using the Sargent bath which uses a chromic anhydride as the main ingredients, and impressing pulse current.

[Claim 2]A chromium plating method distributing an ultrafine particle of insolubility at this bath to the Sargent bath which uses a chromic anhydride as the main ingredients, and carrying out plating processing.

[Claim 3]A chromium plating method carrying out plating processing making the Sargent bath which uses a chromic anhydride as the main ingredients distribute an ultrafine particle of insolubility to this bath, and impressing pulse current further.

[Claim 4]The chromium plating method according to claim 1 or 3, wherein pulses of pulse current to impress are 100 Hz - 3 kHz.

[Claim 5]The chromium plating method according to any one of claims 2 to 4, wherein an ultrafine particle to distribute is aluminum₂O₃ or SiO₂ not more than particle diameter:1micrometer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]About the chromium plating method applied to parts general-industrial-machinery products and at large, especially, it is defect-free and this invention relates to the method of forming the chrome plating tunic excellent in corrosion resistance.

[0002]

[Description of the Prior Art]The industrial chromium plating is applied to the machine part of all fields of industry. The main purpose is use as various slide members by abrasion resistance for ** high hardness tunic to be obtained and ** coefficient of friction being low, and the tribology characteristic being excellent, etc. general chrome plating is obtained from the Sargent bath which uses chromic acid as the main ingredients -- plating liquid composition and plating conditions -- width -- it has the feature from which the tunic of large quality (gloss, hardness, etc.) is obtained. Especially about hardness, it can select arbitrarily in 700-1,100 by Vickers hardness number by changing the degree of plating solution temperature, and current density. These days, it is obtained by addition of organic acid to the thing of 1,500 by Vickers hardness number in plating liquid.

[0003]Thus, on the other hand, the chrome plating coat is holding many technical problems for the corrosion-resistant purpose, although the thing of high hardness is obtained dramatically. That is, although chromium itself is chemically stable, in the case of the plating coat, it has a countless detailed crack of the shape of a tortoise shell. That is, if this coat is used in a wet environment, a corrosion medium will permeate even to a substrate via this crack, and corrosion will occur. When intense, a chrome plating tunic starts bulging by the cubical expansion of the corrosion product of a substrate, and it results in exfoliation development. such -- divide -- the measure which prevents a crack by the measure and (2) fluoridation which carry out minuteness making of the crack by (1) catalyst addition is taken as preventive measures these days.

[0004]

[Problem(s) to be Solved by the Invention]

(1) A thing typical as a method of adding a catalyst has a SRHS bath (Self-Regulating-High-Speed). This bath is a fluoridation bath which used the chromic anhydride as the main ingredients, added K_2SiF_6 to this, and added $SrSO_4$ as a catalyst. However, although the coat of the following problems (with no crack), i.e., ** zero defects, is obtained in plating in this bath, Although the range of fitness plating conditions is dramatically narrow and ** catalyst which a crack generates in a coat in change of few conditions, for example, $SrSO_4$ etc., is added, it does not dissolve in the base bath which uses a chromic anhydride as the main ingredients thoroughly, but this catalyst is floating in the dead of night in the supersaturation state. Therefore, maintaining the always stabilized bath presentation where the concentration of this catalyst changed with prolonged plating, [difficult] ** this bath cannot use the plating equipment which parts other than the plating part which is a fluoridation bath and is a fault of a fluoridation bath are dissolving by corrosion, and are using now for ** fluoridation bath, but needs to invest in plant and equipment newly -- etc. -- there is a problem.

[0005](2) As a method of preventing a crack by fluoridation, the bath which adds fluorides, such as KF, Na_2SiF_6 , and K_2SiF_6 , is in the Sargent bath which uses a chromic anhydride as the main ingredients. It is being unable to prevent a crack perfect as biggest fault in these plating baths, in addition has a fault of being unable to use equipment that parts other than a plating part dissolve by corrosion like said SRHS bath, and present in use.

[0006]By various kinds of plating baths released as present defect-free (with especially no crack) chrome plating as mentioned above, and a method, the actual condition is that there is nothing perfect. This invention tends to provide the method which is stabilized for a long time using the conventional chrome plating equipment, and can form defect-free (there is no crack in particular) chrome plating in view of the above-mentioned state of the art.

[0007]

[Means for Solving the Problem]This invention persons cancel a fault by a chromium plating method released from before, To and the Sargent bath for which a chromic anhydride is used as the main ingredients as a result of carrying out various test and research, in order to attain the technical problem. By making plating liquid distribute an ultrafine particle of insolubility, or using a current wave form at the time of plating as a pulse shape further, it finds out attaining the purpose and came to complete this invention.

[0008]Namely, this invention using the Sargent bath which uses (1) chromic anhydride as the main ingredients, and impressing pulse current. A chromium plating method carrying out plating processing, a chromium plating method distributing an ultrafine particle of insolubility at this bath to the Sargent bath which uses (2) chromic anhydrides as the main ingredients, and carrying out

plating processing, (3) The Sargent bath which uses a chromic anhydride as the main ingredients is made to distribute an ultrafine particle of insolubility to this bath, A chromium plating method carrying out plating processing impressing pulse current furthermore, (4) That an ultrafine particle which carries out a chromium plating method the above (1) by which it is characterized, or given in (3), and (5) distributions of pulses of pulse current to impress being 100 Hz - 3 kHz is aluminum₂O₃ or SiO₂ not more than particle diameter:1micrometer. It is a chromium plating method given in either of above-mentioned (2) - (4) by which it is characterized.

[0009]

[Embodiment of the Invention]The Sargent bath used as the main ingredients the chromic anhydride said to this invention, Generally it is often used and is a plating bath of CrO₃:200-400g/l., CrO₃/H₂SO₄:125:1-1.5, and the presentation that becomes trivalent Cr:2-3g/l. Generally as chrome plating conditions, it is carried out by bath temperature:30-50 ** and current density:20 - 60 A/dm².

[0010]One of the features of this invention is adding the ultrafine particle of insolubility to the Sargent bath which is this base bath. Although an ultrafine particle is generally a thing (hundreds of nm - 1 micrometer or less) and there is no restriction in the smaller one at this invention, since the larger one will act on the minuteness making of a crystal conversely if it is too large not much, its 0.5 micrometer or less is preferred. Although SiO₂ and aluminum₂O₃ is raised as construction material of a concrete ultrafine particle, in this invention, it is not limited to these things, and if it is a thing of insolubility at a chrome plating bath, there will be no restriction in construction material. The gestalt will not be asked if it distributes uniformly during a chrome plating bath, although colloid is most suitable the dispersion state of an ultrafine particle. The quantity which adds an ultrafine particle to a chrome plating bath has the preferred range of 1-100g/l. Namely, the thing which the operation to which the density of the particles which distribute the case of less than 1g/l. during a bath carries out minuteness making of the crystal low falls, It is because problems -- the viscosity of a chrome plating bath becomes large and the inhibition and the good chrome plating coat of the eutectoid of particles accompanying change of pH of the negative pole interface due to the fall of the diffusibility of a under [the chrome plating bath of the hydrogen to generate] are not obtained -- will occur if it becomes in not less than 100g/l.

[0011]Another feature of this invention is carrying out chrome plating, impressing pulse current. As frequency, 100 Hz - several kilohertz are preferably possible in the range of 100 Hz - 3 kHz**. It is because a pulse will become unstable, the waveform at the time of on time one will change and good chrome plating will not be obtained below 100 Hz, if it becomes the growth which the crystal followed, and an operation of minuteness making is not achieved and it is set to not less than 3 kHz.

[0012](OPERATION) An operation of this invention is explained in detail hereafter. The

microphotograph and drawing 2 in which the metal texture of the section of the chrome plating coat by the Sargent bath by which drawing 1 is carried out conventionally, and the surface was shown are the microphotograph in which the metal texture of the section of the chrome plating coat by this invention and the surface was shown. The crack of a large number has generated the conventional thing in a coat so that clearly from drawing 1, but a crack is not observed in the coat of this invention of drawing 2 at all.

[0013]The coat of drawing 2 is obtained on the plating bath composition and plating conditions which are shown in Table 1.

[Table 1]

表1 めっき浴組成、めっき条件

めっき浴組成	めっき条件
CrO ₃ : 250g/リットル	浴 温 : 50℃
CrO ₃ /H ₂ SO ₄ 比: 125:1	電流密度 : 40A/dm ²
3価Cr : 2.5g/リットル	パルス周波数 : 666Hz
SiO ₂ 微粒子 : 50g/リットル	

Here, SiO₂ particles used particle diameter colloidal silica of about 200 nm. The pulse shape made average current density 40 A/dm², and on time one was made into 0.5 m-s, and it made off time 1.0 m-s.

[0014]The operation by using together distributing particles during the plating bath which is the feature of this invention, and a pulse shape is explained to details below. Although not found here about the established theory about the cause of a crack generation of a chrome plating coat, as a result of this invention persons' inquiring by doing examination and research, the cause of a crack of a chrome plating coat can consider the following things. The deposit efficiency of chrome plating is 15 to 20%, and most has energy consumed by hydrogen generating. An electrolysis waveform is a sine wave of a direct current, in that a crystal carries out continuous growth and large-quantity-production hydrogen, the big stress in a precipitated film occurs the dissolution and by carrying out occlusion in a precipitated film at supersaturation, the intensity of a coat stops bearing and going out to this stress, and a crack occurs. That is, it is thought that this crack forms membranes where the crack occurred and overall balance is maintained, if it had generated here and there [of the coat] so that clearly [in a section organization], and the crystal grew to a certain thickness.

[0015]In ** continuation, this invention persons in view of such a phenomenon Relaxation of the

precipitation stress by preventing the crystal growth carried out, ** Various researches were done by the view of relaxation of the precipitation stress by carrying out minuteness making of the precipitated crystal, and it was realized that the growth which continued by addition of the ultrafine particle (insolubility) during the chrome plating bath was prevented as one of the relaxation means of the above-mentioned precipitation stress. That is, if it does in this way, very detailed particles will distribute during a chrome plating bath, will always adsorb or adhere to a deposit side, and crystal growth will be prevented, and a new crystal nucleus will occur. Minuteness making of the crystal by inhibition of the crystal growth which continued by such operation, and generating of an always new crystal is attained. It is a means which prevents the crystal growth which continued by impressing pulse current and using an electrolysis waveform as an interrupted wave form, and carries out minuteness making of the precipitated crystal. Although drawing 3 is the result of measuring the stress in electrodeposits in each chrome plating bath and the stress of about 500 MPa(s) (tensile stress) has occurred in the usual Sargent bath and KF bath, in plating by a pulse shape, it is 250MPa for the minute half [about] of it, and most stress in electrodeposits is in the situation which has not been generated in concomitant use of particle distribution and pulse shape plating further.

[0016]As explained above, by carrying out pulse shape concomitant use with the method and particle distribution which are electrolyzed with a pulse shape by the usual Sargent chrome plating bath, relaxation of stress in electrodeposits was achieved and it became clear that a crack of a coat could be prevented as a result. Although the above-mentioned explanation described concomitant use of ultrafine particle distribution and a pulse shape, but, only the pulse shape is accepted and the effect must not necessarily use it together.

[0017]

[Example]The concrete example of this invention is given hereafter and the effect of this invention is clarified.

[0018](Example 1) In order to investigate the performance of the defect-free chrome plating coat of this invention, two kinds and two kinds of coats for comparison were produced for the plating coat of this invention, the neutral salt spray test was carried out, and anti-corrosiveness was evaluated.

[0019]O The chrome plating coat of this invention : use the Sargent bath which uses chromic acid as the main ingredients for the steel plate of ** substrate SS400, and it is the thing with a plating thickness of 50 micrometers which carried out chrome plating with 50 ** of bath temperature, average current density 40 A/dm², and a pulse shape (on time 0.5 m-s, off time 1.0 m-s).

** Use the Sargent bath which uses chromic acid as the main ingredients for the steel plate of substrate SS400, make this bath carry out 50g [l.] addition distribution of the alumina particle with a mean particle diameter of 0.2 micrometer, and it is the thing with a plating thickness of 50 micrometers which carried out chrome plating at 50 ** of bath temperature, and average current

density 40 A/dm².

** The bath which makes chromic acid the steel plate of substrate SS400 with the main ingredients is made to carry out 50g [l.] addition distribution of the colloidal silica with a mean particle diameter of 300 nm, It is the thing with a plating thickness of 50 micrometers which carried out chrome plating with 50 ** of bath temperature, average current density 40 A/dm², and a pulse shape (on time 0.5 m-s, off time 1.0 m-s).

[0020]O The chrome plating coat for comparison : use the Sargent bath which uses chromic acid as the main ingredients for the steel plate of ** substrate SS400, and it is the thing with a plating thickness of 50 micrometers which carried out chrome plating about the usual chrome plating at 50 ** of bath temperature, and current density 40 A/dm².

** It is the thing with a plating thickness of 50 micrometers which carried out chrome plating at Na₂SiF₆ 4.0g/l., SrSO₄ 2.0g/l., 50 ** of bath temperature, and current density 40 A/dm² to the bath which makes chromic acid the steel plate of substrate SS400 with the main ingredients.

[0021]Shape of the test piece for an examination was used as the plate (100 mm x 100 mm), and a test method and conditions were performed according to JIS-Z2371 (1976). As a result, punctiform rust generated in area the chrome plating coat from the bath to which, as for the usual chrome plating of chrome plating ** for comparison, punctiform rust already added generating, Na₂SiF₆ of **, and SrSO₄ on the whole surface in 24 hours to about 30% in 100 hours. On the other hand, it is generated by punctiform rust in part in a peripheral part for 200 hours at the time, and coat ** of only the pulse shape in the chrome plating coat of this invention is a request, Adding plating coat ** and the colloidal silica particle which added the alumina particle, 500 hours afterward [** / which used the pulse shape together / chrome plating coat], the chrome plating coat of this invention showed the outstanding corrosion resistance not changeful at all.

[0022](Example 2) Plating construction of four kinds of the same chrome plating as an example is carried out at the cylinder rod of the parts for marine vessels, As a result of evaluating in a system environment, in both sides, sea water permeated from the defect of the chrome film in the use for seven days, the substrate was made to corrode, bulging of a coat and exfoliation occurred, and the chrome plating coat for comparison became a situation where use was not borne. On the other hand, it became clear that the chrome plating coat of this invention had the corrosion resistance in which all three persons were excellent completely normal also to the use for one month.

[0023]

[Effect of the Invention]As explained above, according to the chromium plating method of this invention, it can contribute to cost reduction greatly as well as the chrome plating coat which was excellent in corrosion resistance according to zero defects (with no crack) being obtained, including the quality of a product, improvement in productivity, and reduction of the maintenance

inspection work of equipment, and there is industry top value.

[Translation done.]

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TECHNICAL FIELD

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PRIOR ART

[Description of the Prior Art]The industrial chromium plating is applied to the machine part of all fields of industry. The main purpose is use as various slide members by abrasion resistance for ** high hardness tunic to be obtained and ** coefficient of friction being low, and the tribology characteristic being excellent, etc. general chrome plating is obtained from the Sargent bath which uses chromic acid as the main ingredients -- plating liquid composition and plating conditions -- width -- it has the feature from which the tunic of large quality (gloss, hardness, etc.) is obtained. Especially about hardness, it can select arbitrarily in 700-1,100 by Vickers hardness number by changing the degree of plating solution temperature, and current density. These days, it is obtained by addition of organic acid to the thing of 1,500 by Vickers hardness number in plating liquid.

[0003]Thus, on the other hand, the chrome plating coat is holding many technical problems for the corrosion-resistant purpose, although the thing of high hardness is obtained dramatically. That is, although chromium itself is chemically stable, in the case of the plating coat, it has a countless detailed crack of the shape of a tortoise shell. That is, if this coat is used in a wet environment, a corrosion medium will permeate even to a substrate via this crack, and corrosion will occur. When intense, a chrome plating tunic starts bulging by the cubical expansion of the corrosion product of a substrate, and it results in exfoliation development. such -- divide -- the measure which prevents a crack by the measure and (2) fluoridation which carry out minuteness making of the crack by (1) catalyst addition is taken as preventive measures these days.

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EFFECT OF THE INVENTION

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]

(1) A thing typical as a method of adding a catalyst has a SRHS bath (Self-Regulating-High-Speed). This bath is a fluoridation bath which used the chromic anhydride as the main ingredients, added K_2SiF_6 to this, and added $SrSO_4$ as a catalyst. However, although the coat of the following problems (with no crack), i.e., ** zero defects, is obtained in plating in this bath, Although the range of fitness plating conditions is dramatically narrow and ** catalyst which a crack generates in a coat in change of few conditions, for example, $SrSO_4$ etc., is added, it does not dissolve in the base bath which uses a chromic anhydride as the main ingredients thoroughly, but this catalyst is floating in the dead of night in the supersaturation state. Therefore, maintaining the always stabilized bath presentation where the concentration of this catalyst changed with prolonged plating, [difficult] ** this bath cannot use the plating equipment which parts other than the plating part which is a fluoridation bath and is a fault of a fluoridation bath are dissolving by corrosion, and are using now for ** fluoridation bath, but needs to invest in plant and equipment newly -- etc. -- there is a problem.

[0005](2) As a method of preventing a crack by fluoridation, the bath which adds fluorides, such as KF , Na_2SiF_6 , and K_2SiF_6 , is in the Sargent bath which uses a chromic anhydride as the main ingredients. It is being unable to prevent a crack perfect as biggest fault in these plating baths, in addition has a fault of being unable to use equipment that parts other than a plating part dissolve by corrosion like said SRHS bath, and present in use.

[0006]By various kinds of plating baths released as present defect-free (with especially no crack) chrome plating as mentioned above, and a method, the actual condition is that there is nothing perfect. This invention tends to provide the method which is stabilized for a long time using the conventional chrome plating equipment, and can form defect-free (there is no crack in particular) chrome plating in view of the above-mentioned state of the art.

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MEANS

[Means for Solving the Problem] This invention persons cancel a fault by a chromium plating method released from before, To and the Sargent bath for which a chromic anhydride is used as the main ingredients as a result of carrying out various test and research, in order to attain the technical problem. By making plating liquid distribute an ultrafine particle of insolubility, or using a current wave form at the time of plating as a pulse shape further, it finds out attaining the purpose and came to complete this invention.

[0008] Namely, this invention using the Sargent bath which uses (1) chromic anhydride as the main ingredients, and impressing pulse current. A chromium plating method carrying out plating processing, a chromium plating method distributing an ultrafine particle of insolubility at this bath to the Sargent bath which uses (2) chromic anhydrides as the main ingredients, and carrying out plating processing, (3) The Sargent bath which uses a chromic anhydride as the main ingredients is made to distribute an ultrafine particle of insolubility to this bath, A chromium plating method carrying out plating processing impressing pulse current furthermore, (4) That an ultrafine particle which carries out a chromium plating method the above (1) by which it is characterized, or given in (3), and (5) distributions of pulses of pulse current to impress being 100 Hz - 3 kHz is aluminum₂O₃ or SiO₂ not more than particle diameter: 1 micrometer. It is a chromium plating method given in either of above-mentioned (2) - (4) by which it is characterized.

[0009]

[Embodiment of the Invention] The Sargent bath used as the main ingredients the chromic anhydride said to this invention, Generally it is often used and is a plating bath of CrO₃: 200-400g/l., CrO₃/H₂SO₄: 125:1-1.5, and the presentation that becomes trivalent Cr: 2-3g/l. Generally as chrome plating conditions, it is carried out by bath temperature: 30-50 °C and current density: 20 - 60 A/dm².

[0010] One of the features of this invention is adding the ultrafine particle of insolubility to the

Sargent bath which is this base bath. Although an ultrafine particle is generally a thing (hundreds of nm - 1 micrometer or less) and there is no restriction in the smaller one at this invention, since the larger one will act on the minuteness making of a crystal conversely if it is too large not much, its 0.5 micrometer or less is preferred. Although SiO_2 and aluminum $_2\text{O}_3$ is raised as construction material of a concrete ultrafine particle, in this invention, it is not limited to these things, and if it is a thing of insolubility at a chrome plating bath, there will be no restriction in construction material. The gestalt will not be asked if it distributes uniformly during a chrome plating bath, although colloid is most suitable the dispersion state of an ultrafine particle. The quantity which adds an ultrafine particle to a chrome plating bath has the preferred range of 1-100g/l. Namely, the thing which the operation to which the density of the particles which distribute the case of less than 1g/l. during a bath carries out minuteness making of the crystal low falls, It is because problems -- the viscosity of a chrome plating bath becomes large and the inhibition and the good chrome plating coat of the eutectoid of particles accompanying change of pH of the negative pole interface due to the fall of the diffusibility of a under [the chrome plating bath of the hydrogen to generate] are not obtained -- will occur if it becomes in not less than 100g/l.

[0011]Another feature of this invention is carrying out chrome plating, impressing pulse current. As frequency, 100 Hz - several kilohertz are preferably possible in the range of 100 Hz - 3 kHz**. It is because a pulse will become unstable, the waveform at the time of on time one will change and good chrome plating will not be obtained below 100 Hz, if it becomes the growth which the crystal followed, and an operation of minuteness making is not achieved and it is set to not less than 3 kHz.

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OPERATION

(OPERATION) An operation of this invention is explained in detail hereafter. The microphotograph and drawing 2 in which the metal texture of the section of the chrome plating coat by the Sargent bath by which drawing 1 is carried out conventionally, and the surface was shown are the microphotograph in which the metal texture of the section of the chrome plating coat by this invention and the surface was shown. The crack of a large number has generated the conventional thing in a coat so that clearly from drawing 1, but a crack is not observed in the coat of this invention of drawing 2 at all.

[0013]The coat of drawing 2 is obtained on the plating bath composition and plating conditions which are shown in Table 1.

[Table 1]

表1 めっき浴組成、めっき条件

めっき浴組成	めっき条件
CrO ₃ : 250g/リットル	浴 温 : 50℃
CrO ₃ /H ₂ SO ₄ 比: 125:1	電流密度 : 40A/dm ²
3価Cr : 2.5g/リットル	パルス周波数 : 666Hz
SiO ₂ 微粒子 : 50g/リットル	

Here, SiO₂ particles used particle diameter colloidal silica of about 200 nm. The pulse shape made average current density 40 A/dm², and on time one was made into 0.5 m-s, and it made off time 1.0 m-s.

[0014]The operation by using together distributing particles during the plating bath which is the

feature of this invention, and a pulse shape is explained to details below. Although not found here about the established theory about the cause of a crack generation of a chrome plating coat, as a result of this invention persons' inquiring by doing examination and research, the cause of a crack of a chrome plating coat can consider the following things. The deposit efficiency of chrome plating is 15 to 20%, and most has energy consumed by hydrogen generating. An electrolysis waveform is a sine wave of a direct current, in that a crystal carries out continuous growth and large-quantity-production hydrogen, the big stress in a precipitated film occurs the dissolution and by carrying out occlusion in a precipitated film at supersaturation, the intensity of a coat stops bearing and going out to this stress, and a crack occurs. That is, it is thought that this crack forms membranes where the crack occurred and overall balance is maintained, if it had generated here and there [of the coat] so that clearly [in a section organization], and the crystal grew to a certain thickness.

[0015]In ** continuation, this invention persons in view of such a phenomenon Relaxation of the precipitation stress by preventing the crystal growth carried out, ** Various researches were done by the view of relaxation of the precipitation stress by carrying out minuteness making of the precipitated crystal, and it was realized that the growth which continued by addition of the ultrafine particle (insolubility) during the chrome plating bath was prevented as one of the relaxation means of the above-mentioned precipitation stress. That is, if it does in this way, very detailed particles will distribute during a chrome plating bath, will always adsorb or adhere to a deposit side, and crystal growth will be prevented, and a new crystal nucleus will occur. Minuteness making of the crystal by inhibition of the crystal growth which continued by such operation, and generating of an always new crystal is attained. It is a means which prevents the crystal growth which continued by impressing pulse current and using an electrolysis waveform as an interrupted wave form, and carries out minuteness making of the precipitated crystal. Although drawing 3 is the result of measuring the stress in electrodeposits in each chrome plating bath and the stress of about 500 MPa(s) (tensile stress) has occurred in the usual Sargent bath and KF bath, in plating by a pulse shape, it is 250MPa for the minute half [about] of it, and most stress in electrodeposits is in the situation which has not been generated in concomitant use of particle distribution and pulse shape plating further.

[0016]As explained above, by carrying out pulse shape concomitant use with the method and particle distribution which are electrolyzed with a pulse shape by the usual Sargent chrome plating bath, relaxation of stress in electrodeposits was achieved and it became clear that a crack of a coat could be prevented as a result. Although the above-mentioned explanation described concomitant use of ultrafine particle distribution and a pulse shape, but, only the pulse shape is accepted and the effect must not necessarily use it together.

[Translation done.]

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EXAMPLE

[Example]The concrete example of this invention is given hereafter and the effect of this invention is clarified.

[0018](Example 1) In order to investigate the performance of the defect-free chrome plating coat of this invention, two kinds and two kinds of coats for comparison were produced for the plating coat of this invention, the neutral salt spray test was carried out, and anti-corrosiveness was evaluated.

[0019]O The chrome plating coat of this invention : use the Sargent bath which uses chromic acid as the main ingredients for the steel plate of ** substrate SS400, and it is the thing with a plating thickness of 50 micrometers which carried out chrome plating with 50 ** of bath temperature, average current density 40 A/dm^2 , and a pulse shape (on time 0.5 m-s, off time 1.0 m-s).

** Use the Sargent bath which uses chromic acid as the main ingredients for the steel plate of substrate SS400, make this bath carry out 50g [l.] addition distribution of the alumina particle with a mean particle diameter of 0.2 micrometer, and it is the thing with a plating thickness of 50 micrometers which carried out chrome plating at 50 ** of bath temperature, and average current density 40 A/dm^2 .

** The bath which makes chromic acid the steel plate of substrate SS400 with the main ingredients is made to carry out 50g [l.] addition distribution of the colloidal silica with a mean particle diameter of 300 nm, It is the thing with a plating thickness of 50 micrometers which carried out chrome plating with 50 ** of bath temperature, average current density 40 A/dm^2 , and a pulse shape (on time 0.5 m-s, off time 1.0 m-s).

[0020]O The chrome plating coat for comparison : use the Sargent bath which uses chromic acid as the main ingredients for the steel plate of ** substrate SS400, and it is the thing with a plating thickness of 50 micrometers which carried out chrome plating about the usual chrome plating at 50 ** of bath temperature, and current density 40 A/dm^2 .

** It is the thing with a plating thickness of 50 micrometers which carried out chrome plating at Na_2SiF_6 4.0g/l., SrSO_4 2.0g/l., 50 ** of bath temperature, and current density 40 A/dm^2 to the bath which makes chromic acid the steel plate of substrate SS400 with the main ingredients.

[0021] Shape of the test piece for an examination was used as the plate (100 mm x 100 mm), and a test method and conditions were performed according to JIS-Z2371 (1976). As a result, punctiform rust generated in area the chrome plating coat from the bath to which, as for the usual chrome plating of chrome plating ** for comparison, punctiform rust already added generating, Na_2SiF_6 of **, and SrSO_4 on the whole surface in 24 hours to about 30% in 100 hours. On the other hand, it is generated by punctiform rust in part in a peripheral part for 200 hours at the time, and coat ** of only the pulse shape in the chrome plating coat of this invention is a request, Adding plating coat ** and the colloidal silica particle which added the alumina particle, 500 hours afterward [** / which used the pulse shape together / chrome plating coat], the chrome plating coat of this invention showed the outstanding corrosion resistance not changeful at all.

[0022](Example 2) Plating construction of four kinds of the same chrome plating as an example is carried out at the cylinder rod of the parts for marine vessels, As a result of evaluating in a system environment, in both sides, sea water permeated from the defect of the chrome film in the use for seven days, the substrate was made to corrode, bulging of a coat and exfoliation occurred, and the chrome plating coat for comparison became a situation where use was not borne. On the other hand, it became clear that the chrome plating coat of this invention had the corrosion resistance in which all three persons were excellent completely normal also to the use for one month.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The microphotograph in which the metal texture of the section of the plating coat by the Sargent bath currently carried out conventionally and the surface was shown.

[Drawing 2] The microphotograph in which the metal texture of the section of a chrome plating coat and the surface obtained by this invention was shown.

[Drawing 3] The figure showing precipitation stress measurement of the chrome plating coat by this invention, and a comparison chrome plating coat.

[Translation done.]

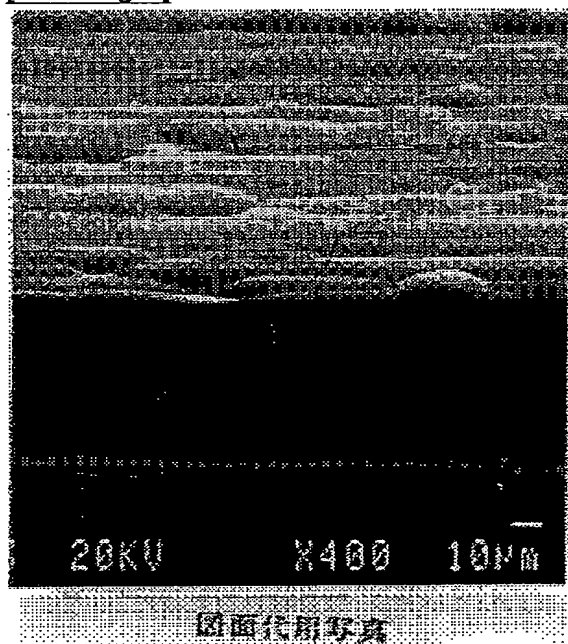
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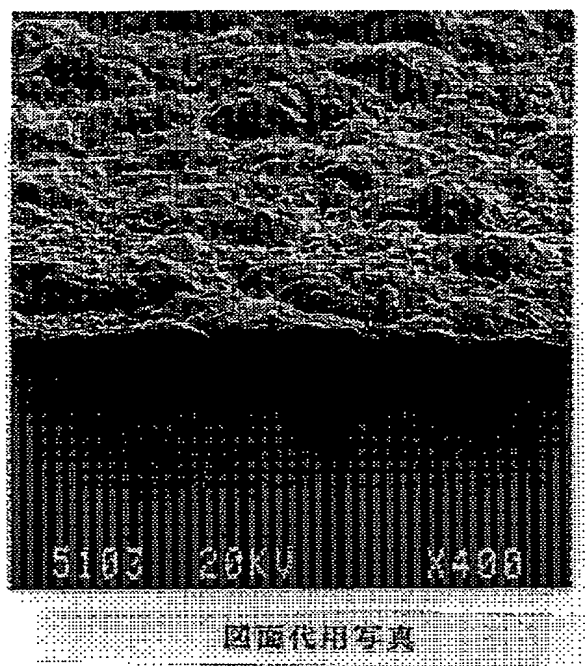
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DRAWINGS

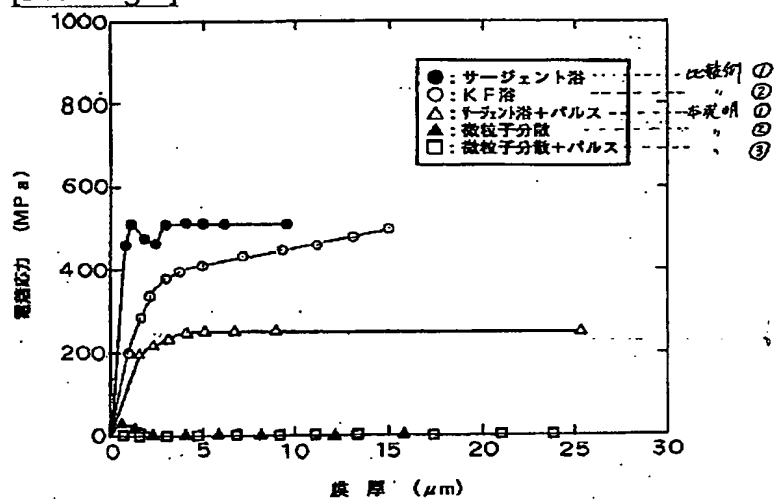
[Drawing 1]



[Drawing 2]



[Drawing 3]



電張応力測定結果 (スパイラル応力計, SUS304)

[Translation done.]